

SPECIFICATION

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ELECTROLYTIC PROCESS AND APPARATUS

Cross Reference to Related Applications

This application claims priority to U.S. Provisional Application Serial No. 60/345,307, filed on October 22, 2001, and U.S. Provisional Application Serial No. 60/369,090, filed on March 29, 2002, which are incorporated herein by reference in their entireties.

Background of Invention

[0001] This disclosure relates to electrolysis and more particularly, relates to improved electrolytic processes and apparatuses for the oxidation of inorganic or organic species.

[0002] With the decline of gaseous chlorine as a microbiocide, various alternatives have been explored, including bleach, bleach with bromide, bromo-chlorodimethyl hydantoin, ozone, and chlorine dioxide (ClO_2). Of these, chlorine dioxide has generated a great deal of interest for control of microbiological growth in a number of different industries, including the dairy industry, the beverage industry, the pulp and paper industries, the fruit and vegetable processing industries, various canning plants, the poultry industry, the beef processing industry and miscellaneous other food processing applications. Chlorine dioxide is also seeing increased use in municipal potable water treatment facilities and in industrial waste treatment facilities, because of its selectivity towards specific environmentally-objectionable waste materials, including phenols, sulfides, cyanides, thiosulfates, and mercaptans. In addition, chlorine dioxide is being used in the oil and gas industry for downhole applications as a well stimulation enhancement additive.

[0003]

Unlike chlorine, chlorine dioxide remains a gas when dissolved in aqueous

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[0004] The biocidal activity of chlorine dioxide is believed to be due to its ability to penetrate bacterial cell walls and react with essential amino acids within the cell cytoplasm to disrupt cell metabolism. This mechanism is more efficient than other oxidizers that "burn" on contact and is highly effective against legionella, algae and amoebal cysts, giardia cysts, coliforms, salmonella, shigella, and cryptosporidium.

[0005] Unfortunately, chlorine dioxide in solution is unstable with an extremely short shelf life and thus, is not commercially available. Chlorine dioxide must typically be generated at its point of use such as, for example, by a reaction between a metal chlorate or metal chlorite in aqueous solution and a strong acid.

[0006] Electrochemical processes provide a means for generating chlorine dioxide for point of use applications. For example, U.S. Patent No. 5,419,816 to Sampson et al. describes a packed bed ion exchange electrolytic system and process for oxidizing species in dilute aqueous solutions by passing the species through an electrolytic reactor packed with a monobed of modified cation exchange material. A similar electrolytic process is described in U.S. Patent No. 5,609,742 to Sampson et al. for reducing species using a monobed of modified anion exchange.

[0007] One difficulty with electrochemical processes is that it can be difficult to control the generation of undesirable species. For example, there are many electrochemical reactions that can occur at the anode. Within a potential range of 0.90 to 2.10 volts, at least eight different reactions are thermodynamically possible, producing products such as chlorate (ClO_3^-), perchlorate (ClO_4^-), chlorous acid (HClO_2), oxygen (O_2), hydrogen peroxide (H_2O_2) and ozone (O_3). It is highly desirable and a significant commercial advantage to achieve high yield efficiency without producing these undesirable side reactions.

[0008] Chlorine dioxide has also been produced from a chlorine dioxide precursor

ceramic particle to a temperature effective to form a metal oxide.

- [0014] A process for generating chlorine dioxide from an alkali metal chlorite solution comprises applying a current to the electrolytic reactor, wherein the electrolytic reactor includes an anode, a cathode, and a catalyst material; flowing an aqueous alkali metal chlorite solution into the electrolytic reactor; and contacting the alkali metal chlorite solution with the catalyst material to electrocatalytically produce an effluent containing chlorine dioxide.
- [0015] In another embodiment, a process for generating chlorine dioxide from an alkali metal chlorite solution includes applying a current to an electrolytic reactor including an anode compartment comprising an anode and a catalyst material; and a cathode compartment comprising a cathode; flowing an aqueous alkali metal chlorite solution into the electrolytic reactor; and contacting the alkali metal chlorite solution with the catalyst material to electrocatalytically produce an effluent containing chlorine dioxide.
- [0016] In another embodiment, a process for generating chlorine dioxide from an alkali metal chlorite solution comprises applying a current to an electrolytic wherein the electrolytic reactor includes an anode compartment comprising an anode, a cathode compartment comprising a cathode, and a central compartment disposed between the anode and cathode compartments, wherein the central compartment comprises a catalyst material; flowing water into the anode compartment and generating hydrogen atoms; passing the hydrogen atoms into the central compartment; flowing the alkali metal chlorite solution into the central compartment; and contacting the alkali metal chlorite solution with the catalyst material to produce an effluent containing chlorine dioxide.
- [0017] In another embodiment, a process for generating chlorine dioxide from a dilute alkali metal chlorite solution comprises applying a current to an electrolytic reactor, wherein the electrolytic reactor comprises an anode compartment comprising an anode, a cathode compartment comprising a cathode, and a central compartment disposed between the anode and cathode compartments, wherein the central compartment comprises a catalyst material, and wherein a non-permselective membrane separates the anode compartment from the central compartment; flowing

water into the anode compartment and generating hydrogen atoms; passing the hydrogen atoms into the central compartment; flowing the dilute alkali metal chlorite solution into the central compartment; and contacting the dilute alkali metal chlorite solution with the catalyst material to produce an effluent containing chlorine dioxide.

[0018] The above described and other features will become better understood from the detailed description that is described in conjunction with the accompanying drawings.

Brief Description of Drawings

- [0019] Referring now to the figures wherein the like elements are numbered alike:
- [0020] Figure 1 shows a cross sectional view illustrating a packed bed electrolytic reactor;
- [0021] Figure 2 shows a partial cross sectional view illustrating the anode compartment of Figure 1, wherein the particulate material is layered;
- [0022] Figure 3 shows a cross sectional view illustrating another packed bed electrolytic reactor;
- [0023] Figure 4 shows a partial cross sectional view illustrating the central compartment of Figure 3, wherein the particulate material is layered;
- [0024] Figure 5A and 5B show an exploded isometric view of an electrolytic reactor cassette;
- [0025] Figure 6 is a graph showing a pressure drop of an electrolytic reactor as a function of time for different catalyst support materials;
- [0026] Figure 7 is a graph showing conversion efficiency of an electrolytic reactor as a function of time during the electrolytic production of chlorine dioxide from an aqueous sodium chlorite feed solution;
- [0027] Figure 8 is a graph showing a comparison of conversion efficiencies for different electrolytic reactors; and
- [0028] Figure 9 is a graph showing a comparison of the applied voltage level as a function of time for different electrolytic reactors.

106, respectively, are selected to be non-permselective membranes.

[0035] The anode compartment 102 includes an anode 112 and preferably, is filled with particulate material 108. The cathode compartment 106 includes a cathode 114 and preferably, is filled with particulate material 108. The anode 112 and the cathode 114 are in electrical communication with a source of direct current 115 (DC). The central compartment 104 is filled with particulate material 108.

[0036] In one embodiment, the central compartment 104 is filled with the catalyst material or a mixture of the catalyst material and the cation exchange material.

[0037] In another embodiment, the anode and cathode compartments 102, 106 are filled with the cation exchange material and the central compartment 104 is filled with the catalyst material or a mixture of the catalyst material and the cation exchange material.

[0038] In another embodiment, each compartment 102, 104, and 106 includes the catalyst material or a mixture of the catalyst material and the cation exchange material.

[0039] In a preferred embodiment, the particulate material 108 in the central compartment 104 is arranged in layers. As previously discussed, the number of layers can vary. Preferably, the total number of layers is about 1 to about 12, with about 2 to about 6 more preferred, and about 3 to about 4 even more preferred. For example, as shown in Figure 4, the particulate material 108 may be layered in the central compartment 104 in three equal layers 109, 110, and 111. Preferably, the bottommost layer 111 is filled with cation exchange material, the middlemost layer 110 is filled with about an equal mixture of catalyst material and cation exchange material, and the uppermost layer 109 is filled with catalyst material. In this configuration, it is preferred that the solution flow upwardly through the particulate material from the bottommost layer 111 to the uppermost layer 109.

[0040] Referring now to Figures 5A and 5B, there is shown an exploded isometric view of an exemplary electrolytic reactor cassette 130 employing the three compartments 102, 104, 106, shown in Figure 2. The cassette is formed from stock materials that are preferably chemically inert and non-conductive. Components forming the cassette

[0044] While the arrangements of anode, cathode, and packed bed electrolytic reactors illustrated in Figures 1, 2, and 3 are presently considered preferable, any arrangement in which a sufficient quantity of particulate material (including catalyst material) is packed between the anode and cathode in an electrolytic reactor or in at least one of the compartments of a divided electrolytic reactor can be used. Other embodiments include, but are not limited to, separation of the anode and cathode compartments to control intermixing of gases and solutions and provision of any number of packed-bed compartments separated by membranes placed between the anode and cathode to affect other oxidation, reduction or displacement reactions.

[0045] The anodes 12, 112 and the cathodes 14, 114 may be made of any suitable material based primarily on the intended use of the electrolytic reactor, costs and chemical stability. For example, the anode may be made of a conductive material, such as ruthenium, iridium, titanium, platinum, vanadium, tungsten, tantalum, oxides of at least one of the foregoing, combinations including at least one of the foregoing, and the like. Preferably, the anode comprises a metal oxide catalyst material disposed on a suitable support. The supports are typically in the form of a sheet, screen, or the like and are formed from a rigid material such as titanium, niobium, and the like. The cathode may be made from stainless steel, steel or may be made from the same material as the anode.

[0046] Permselective membranes, e.g., 20, 116, 118, preferably contain acidic groups so that ions with a positive charge can be attracted and selectively passed through the membrane in preference to anions. Preferably, the permselective membrane contains strongly acidic groups, such as R-SO_3^- and is resistant to oxidation and temperature effects. In a preferred embodiment, the permselective membranes are fluoropolymers that are substantially chemically inert to chlorine dioxide and the materials or environment used to produce the chlorine dioxide. Examples of suitable permselective membranes include perfluorosulfonate cation exchange membranes commercially available under the trade name NAFION commercially available from E.I. duPont de Nemours, Wilmington, DE.

[0047] Non-permselective membranes e.g., 20, 116, 118, contain pores that permit the non-selective diffusion of ionic species as well as non-ionic species from one

10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706

[0049] As previously noted, the term "particulate material" (e.g., 18, 24, 108) refers to the cation exchange material and/or the catalyst support material. The cation exchange material is preferably an oxidizing exchanger, i.e., a cation exchange resin. During operation of the electrolytic reactor 10, 100, 130, it is hypothesized that the function of the cation exchange material includes, among others, electro-actively exchanging or adsorbing alkali metal ions from an aqueous alkali metal chlorite solution and releasing hydrogen ions. The released hydrogen ions can then be used to regenerate the cation exchange material back to the hydrogen form thereby releasing alkali metal

ions or the like that may then pass into the cathode compartment, if present. The use of the cation exchange material is especially useful when feeding a dilute alkali metal chlorite solution into compartment 16 or 104, as it helps lower the voltage within the compartment and increases conversion efficiency. The term "dilute" refers to aqueous alkali metal chlorite solutions containing less than about 10,000 milligrams alkali metal chlorite per liter of solution (mg/L), preferably less than about mg/L, and more preferably less than about 1,500 mg/L.

[0050] Examples of suitable cation exchange materials include, but are not intended to be limited to, polystyrene divinylbenzene cross-linked cation exchangers (e.g., strong acid types, weak acid types, iminodiacetic acid types, chelating selective cation exchangers and the like); strong acid perfluorosulfonated cation exchangers; naturally occurring cation exchangers, such as manganese greensand; high surface area macro-reticular or microporous type ion exchange resins having sufficient ion conductivity, and the like. For example, strong acid type exchange materials suitable for use are commercially available from Mitsubishi Chemical under the trade names Diaion SK116 and Diaion SK104. Optionally, the cation exchange material may be further modified, wherein a portion of the ionic sites are converted to semiconductor junctions, such as described in U.S. Patent Nos. 6,024,850, 5,419,816, 5,705,050 and 5,609,742, herein incorporated by reference in their entireties. In a preferred embodiment, the cation exchange materials have a cross-linking density greater than about 8 %, with greater than about 12 % more preferred and with greater than about 16 % even more preferred. Increasing the cross-linking density of the cation exchange materials has been found to increase the resistance of the cation exchange materials to oxidation and degradation. As a result, operating lifetimes for the electrolytic reactor can advantageously be extended during use for the production of strongly oxidizing products such as chlorine dioxide.

[0051] The particulate cation exchange material may also include electrically conductive particles, such as carbon and the like. The electrically conductive particles can be used to affect the transfer of DC current from the electrode to the membrane. For example, the use of electrically conductive particles can be used to lower the electrical resistance within the compartment. However, some additives, such as carbon, are prone to disintegration in acidic environments, thus requiring careful selection.

[0052] The packing density and conductivity of the cation exchange material within the compartment can be adjusted depending on the operating parameters and desired performance for the electrolytic reactors 10, 100, 130. For example, the cation exchange material may be shrunk before use in the electrolytic reactor, such as by dehydration or electrolyte adsorption. Dehydration may be by any method in which moisture is removed from the ion exchange material, for example, using a drying oven. It has been found that dehydration prior to packing can increase the packing density by as much as 40 %. Electrolyte adsorption involves soaking the material in a salt solution, such as sodium chloride. The packing density of the material so treated can be increased by as much as 20 %. The increase in packing density advantageously increases the volume in which the DC current travels, thus reducing the electrical resistance in the electrolytic reactor.

[0053] The catalyst material preferably comprises a support and an active metal catalyst. Preferably, the active metal catalyst is finely and discretely deposited onto the support. While not wanting to be bound by theory, it is believed that the active metal catalyst adsorbs hydrogen atoms without reacting with the hydrogen atoms, which form stable hydrides. Preferably, the active metal catalyst does not adsorb hydrogen atoms into its crystal lattice since this will decrease its catalytic activity. In a preferred embodiment, the active metal catalyst is a noble metal and does not react or dissolve with any of the components or solutions used in the electrolytic reactor 10, 100. While not wanting to be bound by theory, it is believed that the catalytic activity of the active metal is associated with crystal imperfections and the finely divided deposits help to increase the surface area as well as increase the number of active catalytic sites. Suitable active metal catalysts include, but are not limited to, ruthenium, platinum, palladium, osmium, iridium, rhodium, titanium, manganese, lead, zirconium, niobium, tantalum, tungsten, tin, and composites or mixtures or alloys or oxides of at least one of the foregoing metal catalysts. Preferably, the active metal catalyst is an oxide of a metal selected from the group consisting of ruthenium, platinum, palladium, osmium, iridium, and rhodium. More preferably, the active metal catalyst is a platinum oxide.

[0054] In another embodiment, the active metal catalyst is a combination of an oxide of ruthenium, platinum, palladium, osmium, iridium, rhodium or mixtures or alloys of at least one of the foregoing and a less active oxide of a metal including titanium, lead,

manganese, zirconium, niobium, tantalum, tungsten, tin or mixtures or alloys of at least one of the foregoing. Preferably, the molar ratio of the active metal catalyst to the less active metal catalyst is of about 0.3 : 1 to about 100 : 1. More preferably, the molar ratio of the active metal catalyst to the less active metal catalyst is about 10 : 1.

[0055] Preparation of the catalyst material generally includes contacting the support with a catalyst precursor to form the active metal catalyst sites, for example, a catalyst precursor salt. In one embodiment, a metal oxide precursor salt is dissolved in an aqueous solution including an alcohol, and the solution is coated onto the support. Suitable alcohols include methanol, ethanol, isopropanol, propanol, butanol, combinations including at least one of the foregoing alcohols, and the like. In a preferred embodiment, the metal oxide precursor salt is dissolved in isopropanol and deionized water solution. The amount of alcohol used in the solution is dependent on the solubility of the metal oxide precursor salt, wherein the volume fraction of alcohol in an aqueous solution is about 30 to about 90 % (v/v), with about 40 to about 80 % (v/v) preferred and with about 50 to about 60 % (v/v) more preferred.

[0056] Depending on the desired properties, a solution of the metal oxide precursor salt may contain further additives, for example, ions that increase the solubility of the metal oxide precursor. Suitable ions include hydroxides, chlorides, phosphates, sulfates, ammonium, potassium, sodium, lithium or the like. Preferably, the additive is ammonium hydroxide. The weight fraction of additive in the solution is about 0.1 to about 10 % (w/v), with about 0.5 to about 5 % (w/v) preferred and with about 1 % (w/v) more preferred.

[0057] Alternatively, the metal catalyst may be deposited onto the support material using other techniques such as impregnation, co-precipitation, ion exchange, dipping, spray coating, vacuum deposition, sputtering or the like. Preferably, the amount of metal catalyst deposited onto the support is about 0.01 to about 100-weight %, with about 0.01 to about 10-weight % more preferred, and with about 0.05 to about 2-weight % most preferred. In addition, it has been found that the catalyst activity of the catalyst material is improved with multiple depositions, i.e., the metal oxide precursor solution is applied by several individual depositions. Preferably, the number of depositions is about 2 to about 12, with the number of depositions of about 2 to about 3 more

preferred.

[0058] The metal deposited onto the support by the precursor solution is then thermally or chemically oxidized to the oxide form. When utilizing a thermal process, adjusting the temperature can control the extent of oxidation. The support is preferably thermally stable to the oxidation temperatures employed. The oxidation temperatures are preferably about 200 °C to about 1000 °C, with about 400 °C to about 800 °C more preferred, and with about 500 °C to about 700 °C even more preferred. Suitable chemical oxidants include permanganate. The extent of oxidation may be increased when a multiple deposition process is used in contrast to a single deposition process.

[0059] Suitable supports for the catalyst material include metals, zeolites, anthracite, glauconite, faujasite, mordenite, clinoptilolite, aluminas, silicas, clays, ceramics, carbon and the like. Of these supports, ceramics are most preferred. In a preferred embodiment, the catalyst materials are made from those ceramics described in U.S. Patents 4,725,390 and 4,632,876, herein incorporated by reference in their entireties. Preferred ceramics are those made essentially from nonmetallic minerals (such as mineral clays) by firing at an elevated temperature. More preferred are ceramic materials commercially available under the trade name MACROLITE[®] by the Kinetico Company. The MACROLITE[®] ceramic materials are spherically shaped and characterized by having a rough texture, high surface area, and level of moisture absorption of less than about 0.5%. The low level of moisture absorption allows for the metal oxide precursor solution to penetrate a minimal depth into the surface of the ceramic, thereby depositing metal onto the external surface of the support, an optimum location for subsequent contact with an aqueous solution. The surface area of the MACROLITE[®] ceramic materials is believed to be on the order of about 103 m² per gram.

[0060] The process for making ceramic support materials, such as the MACROLITE[®] material, generally includes the following steps. In the first step, mineral particulate, binder, silicon carbide, and parting agent are mixed and spheroidized in order to form unfired spheroids. One example of mineral particulates contains: 60% orthoclase, 10% nepheline, 10% hornblende, 5% diopside, 15% accessory minerals (titanite, apatite,

magnetite and biotite) and trace amounts of secondary minerals (e.g. kaolinite and analcite). Another example contains approximately 75% plagioclase and orthoclase feldspar and 25% of the minerals pyroxene, hornblende, magnetite and quartz of which magnetite is less than 5%. Byproduct mineral fines of perlite (containing 2–5% chemically bound water) will also function as the mineral particulates. Minerals containing chemically bound water or sulfur, which are useful components of the mineral particulates, are hornblende, apatite, biotite, pyrite, vermiculite and perlite.

[0061] Binders that may be useful as raw materials include bentonite starch, polyvinyl alcohol, cellulose gum, polyvinyl acetate and sodium lignosulphonate. The amount of binder may generally comprise about 1 to about 5% by weight of the dry materials fed to the mixer and is generally sufficient to permit screening and handling of the spheroids without significant attrition or breakage.

[0062] Suitable parting agents include magnesium oxide, zircon, diaspore and high alumina clays as well as other surface metal oxides.

[0063] The spheroids are then dried at a temperature of about 40 °C to about 200 °C and typically screened. The ceramic spheroids are then over-fired in a kiln, which allows for the formation of the internal air cells, making the finished product less dense. The firing atmosphere is typically air. The silicon carbide in the spheroids is oxidized during firing, the SiC near the surface being more extensively oxidized than that in the core.

[0064] The product from the kiln is screened using standard methods known to those skilled in the art. Either before, during or after the screening step, the fired spheroids may be subjected to vigorous agitation by air or some other agitation means or to a water washing step in order to remove dust from their surfaces. The support material is then coated with an active metal catalyst in the manner previously described.

[0065] The particulate material, i.e., the cation exchange material or the catalyst material, is not intended to be limited to any particular shape. Suitable shapes include rods, extrudates, tablets, pills, irregular shaped particles, spheres, spheroids, capsules, discs, pellets or the like. In a preferred embodiment, the particulate material is spherical. More preferably, the particulate material includes a reticulated and textured

surface having an increased surface area. The size of the particulate material is dependent on the acceptable pressure drop across the bed of particulate material. The smaller the particulate material, the greater the pressure drop.

[0066] The size of the particulate material is generally defined by a mesh size of a sieve in which the particles are screened. For example, a 30 mesh sieve will allow particles less than about 600 micrometers to pass through the sieve, whereas particles about 600 micrometers or larger than will not pass through. Generally, sieves of varying mesh ratings are stacked and particles are separated using methods well known to those skilled in the art. The range of particles separated is defined by the mesh size of the sieves used. For example, a mesh size designation of 20/40 means that substantially all particles have a size ranging from 20 to 40 mesh (about 841 to about 420 micrometers in diameter). A 30/50 designation indicates that substantially all particles have a size ranging from 30 to 50 mesh (about 595 to about 297 micrometers in diameter). The sizes of the particulate matter are preferably smaller than 7 mesh (about 2800 micrometers in diameter), with smaller than 14 mesh (about 1400 micrometers in diameter) more preferred, and with smaller than 30 mesh (about 595 micrometers in diameter) even more preferred. Also preferred are particulate sizes greater than 60 mesh (about 250 micrometers in diameter), with greater than 50 mesh (about 297 micrometers in diameter) more preferred, and greater than 40 mesh (about 425 micrometers) even more preferred.

[0067] In a preferred mode of operation, a dilute aqueous feed solution of an alkali metal chlorite solution is passed through a selected compartment of the electrolytic reactor to generate an effluent containing chlorine dioxide. For example, in electrolytic reactor 100, the alkali metal chlorite solution preferably flows through central compartment 104. Water flows through the cathode and anode compartments 102, 106, respectively. Preferably, the water is deionized. As a current is applied to the reactor 100, the anode compartment 102 oxidizes the water to generate, among others, hydrogen ions whereas the cathode compartment 106 reduces the water to generate, among others, hydroxyl ions. The hydrogen ions generated in the anode compartment 102 can diffuse through membrane 116 into the central compartment 104. The hydrogen ions can be used to regenerate the cation exchange resin, if present, within the central compartment 104. Oxidation of the dissociated hydrogen

ions into hydrogen atoms transpires so that the electrochemical oxidation of chlorite ions to chlorine dioxide can occur. The applied current to the reactor 100 should be sufficient to reduce the pH of the resulting chlorine dioxide effluent solution to less than about 7. More preferably, the pH is reduced to about 1 to about 5, with a reduction of pH to about 2 to about 3 most preferred. The alkali metal ions from the alkali metal chlorite solution can diffuse through membrane 118 to the cathode compartment 106 and with the hydroxyl ions produce an alkali metal hydroxide effluent from the cathode compartment 106.

[0068] In electrolytic reactor 10, the alkali metal chlorite solution flows through the anode compartment 16. As a current is applied to the reactor 10, the anode compartment 16 oxidizes the solution to generate, among others, hydrogen ions. As previously described, oxidation of the dissociated hydrogen ions into hydrogen atoms transpires so that the electrochemical oxidation of chlorite ions to chlorine dioxide can then occur.

[0069] The concentration of chlorine dioxide produced by the electrolytic reactor, e.g. 10, 100, is preferably less than about 6.0 grams per liter (g/L), with less than about 3 g/L more preferred and less than about 0.65 g/L even more preferred. Also preferred is a chlorine dioxide concentration greater than about 0.06 g/L, with greater than about 0.3 g/L more preferred and greater than about 0.5 g/L even more preferred. At concentrations greater than about 6.0 g/L, there is an increased risk of producing chlorine dioxide in the vapor phase, which undesirably can cause an explosion referred to by those skilled in the art as a "puff".

[0070] There are a number of variables that may be optimized during operation of the electrolytic reactor. For example, current density is preferably maintained at about 5 to about 100 milliAmps per square centimeter (mA/cm^2). More preferably, the current density is less than about $50 \text{ mA}/\text{cm}^2$, with less than about $35 \text{ mA}/\text{cm}^2$ even more preferred. Also preferred, are current densities greater than about $10 \text{ mA}/\text{cm}^2$, with greater than about $25 \text{ mA}/\text{cm}^2$ more preferred. The temperature at which the aqueous medium is maintained during contact of the alkali metal chlorite solution with the catalyst can vary widely. Preferably, the temperature is less than about 50°C , with less than about 35°C more preferred and with less than about 25°C even more preferred.

$^{\circ}\text{C}$ even more preferred. Also preferred is a temperature greater than about 2°C , with greater than about 5°C more preferred, and with greater than about 10°C even more preferred. In a preferred embodiment, the process is carried out at ambient temperature.

[0071] In addition to temperature and current density, the contact time of the chlorine dioxide precursor with the catalyst material is preferably less than about 20 minutes and more preferably, less than about 2 minutes. Also preferred is a contact time greater than about 1 minute, with greater than about 0.1 minute more preferred. The velocity of the chlorine dioxide precursor solution through the catalyst bed is preferably less than about 100 centimeters/minute (cm/min), with less than about 70 cm/min more preferred and less than about 30 cm/min more preferred. Also preferred is a velocity greater than about 0.1 cm/min, with greater than about 10 cm/min more preferred and with greater than about 20 cm/min even more preferred. The pressure drop through the catalyst bed is preferably less than about 20 pounds per square inch (psi) and for most applications, with less than about 10 psi more preferred. Also preferred is a pressure drop greater than about 0.1 psi, and for most applications, with greater than about 1 psi more preferred. Further optimization for any of these process variables is well within the skill of those in the art in view of this disclosure.

[0072] While not wanting to be bound by theory, the use of the catalyst material in the electrochemical reactor system effectively lowers the activation energy for the oxidation of dissociated hydrogen ions into hydrogen atoms. Oxidation of the dissociated hydrogen ions into hydrogen atoms transpires so that the electrochemical oxidation of chlorite ions to chlorine dioxide can occur. It is believed that the electrochemical production of chlorine dioxide from chlorite ions is believed to proceed in accordance with the following reaction scheme:



[0073] Based on this reaction scheme, the maximum yield efficiency of chlorine dioxide will be an 80% conversion. Moreover, in addition to generating chlorine dioxide, the reaction advantageously produces as a byproduct, chloride ions. Chloride ions are not toxic or hazardous for most applications requiring the in situ generation of chlorine

dioxide.

[0074] In electrolytic reactors employing a non-permselective membrane to separate the anode compartment from the central compartment, the use of dilute chlorite solutions as described herein and the hygroscopic nature of the non-permselective membrane minimizes diffusion of the chlorite ions from the central compartment to the electrode compartments. Moreover, it is believed that employing cation exchange resins in the anode and/or cathode compartments further minimizes diffusion of chlorite ions from the central compartment to the respective electrode compartment. As a result, conversion efficiency of chlorite ion to chlorine dioxide is close to or about the maximum conversion efficiency.

Example 1.

[0075] In this example, a ceramic catalyst material was prepared as follows. A metal oxide precursor solution was prepared by admixing 0.85 grams tetraamineplatinum (II) chloride, 41 ml of 91% isopropyl alcohol, 0.83 ml of 30% ammonium hydroxide and 26 ml of deionized water. The precursor solution was used twice to coat 100 milliliters of MACROLITE ML-20/40 that had been backwashed and air dried for about 12 hours. After each coating, the resin was baked at 550 ° C for 30 minutes.

Example 2.

[0076] In this example, a ceramic catalyst material was prepared as follows. A metal oxide precursor solution was prepared by admixing 0.85 grams tetraamineplatinum (II) chloride, 41 ml of 91% isopropyl alcohol, 0.83 ml of 30% ammonium hydroxide and 26 ml of deionized water. The precursor solution was used twice to coat 100 milliliters of SIR-600 resin commercially available from ResinTech, Inc. that had been backwashed and air-dried for about 12 hours. After each coating, the resin was baked at 550 ° C for 30 minutes.

Example 3.

[0077] In this example, electrochemical reactor cassettes were configured as described in Figures 4 and 5. The electrode compartments contained SK116 cation exchange resin commercially available from Mitsubishi Chemical. The central compartment contained

a particulate material bed of three equal layers. The first layer consisted of SK116 cation exchange resin; the second layer consisted of equal amounts by weight of the SK116 cation exchange resin and the catalyst material; and the third layer consisted of the catalyst material. The catalyst material was prepared in accordance with Examples 1. An overview of the cassette components is shown in Table I.

[t3]

Table I.

Anode	DSA, flat sheet
Cathode	316L stainless steel, flat sheet
Electrode Area	155 cm ²
Membrane Area	155 cm ²
Inter Membrane Spacing	1.27 cm
Catalyst	Pt impregnated (Example 1)
Cation Exchange Resin	SK116 (Mitsubishi Chemical)
Cation Exchange Membrane	CMI-7000 (Membranes International, Inc.)

[0078] Four cassettes containing the ceramic catalyst material were installed in parallel in a HALOX 1000 chlorine dioxide generator. Performance for the electrolytic reactor system was monitored for 1000 hours, wherein each data point was taken at 100-hour intervals. A continuous stream of softened water having a conductivity of 120 μ S/cm was passed through each compartment at a rate of 150 mL/minute and a temperature of 25 °C. Sodium chlorite at a concentration of 25% (wt/wt) was injected into the stream flowing into the central compartment at a flow rate such that the concentration of sodium chlorite was approximately 1000 mg/L (the maximum chlorine dioxide yield based on the chlorite concentration is 746mg/L). The temperature of the sodium chlorite solution was maintained at about 25 °C and was first passed through the first layer of the central compartment. A constant current of about 4.0 amps was applied to each cassette.

[0079] Figure 6 illustrates the pressure drop (pressure/flow rate) through the central compartment as a function of time. An increase in pressure drop is an indication that compaction of the bed within the central compartment is occurring. The use of the electrolytic reactor employing the catalyst material did not result in a pressure increase during continuous operation of the reactor for 1000 hours. Rather, the results show that the pressure drop was constant throughout the period of operation suggesting that compaction of the bed did not occur. A visual inspection of a disassembled cassette showed no evidence of compaction or channeling.

[0080] Figure 7 graphically depicts the conversion efficiency as a function of time. A Direct Reading Spectrophotometer, Model No. DR/2000, was used to measure the chlorine dioxide concentration (mg/L) in the exiting solution using Hach Company Method 8138. Measurement of the yield provides a standard for evaluating actual performance of the cassette and can be determined in accordance with the following mathematical relationship:

$$\%Yield = \frac{actual}{theoretical} \times 100$$

wherein the actual yield is determined from the amount of chlorine dioxide generated, and wherein the theoretical yield is calculated by the amount of chlorine dioxide that could be generated from the sodium chlorite solution. As previously discussed, since it takes five moles of chlorite ions to make 4 moles of chlorine dioxide, the theoretical yield can be calculated as follows:

$$\%TheoreticalYield = \frac{[ClO_2]_{product}}{\left[\frac{4}{5}\right][NaClO_2]_{feed} \left[\frac{90.5}{67.5}\right]} \times 100$$

wherein the term (90.5/67.5) is the ratio of the equivalent weight of the sodium chlorite to chlorine dioxide.

[0081] As shown in Figure 7, the conversion efficiency for the cassette employing the ceramic material is constant at about greater than about 95% of the maximum theoretical yield during the 1000 hours of continuous operation. Thus, the use of the catalyst material in the electrolytic reactor provides a yield that is at about the maximum possible yield. Increased conversion efficiencies over a prolonged period of time are a significant commercial advantage since it reduces the maintenance and operating costs of these reactors significantly.

Example 4.

[0082]

In this example, two electrochemical reactor cassettes were configured as described in Figures 4 and 5. Each cassette included electrode compartments that contained SK116 cation exchange resin, wherein each compartment was separated from an adjacent compartment by cation exchange membranes (permselective). The central compartment of the first cassette contained a particulate material bed of three

equal layers. The first layer consisted of SK116 cation exchange resin; the second layer consisted of equal amounts by weight of the SK116 cation exchange resin and a ceramic catalyst material; and the third layer consisted of the ceramic catalyst material. The ceramic catalyst material was prepared in accordance with Example 1. The central compartment of the second cassette contained a packed bed of Diaion SK1B cation exchange resin. Commercially available from Mitsubishi Chemical, Diaion SK1B is a cross-linked polystyrene cation exchange resin having a cross-linking density of 8%.

[0083] Softened water was passed upwardly through the anode compartment at a flow rate of about 150 mL/min. A 25-weight % of sodium chlorite solution was added to the effluent of the anode compartment such that the final concentration of sodium chlorite was about 1000 mg/L. The combined sodium chlorite/effluent solution was then passed through the catalyst compartment. In the compartment including the three layers, the fluid passed from the bottommost layer to the topmost layer. In addition, softened water was passed upwardly through the cathode compartment at a flow rate of about 50 mL/min. While passing the solutions through the compartments of the reactor, a controlled current of about 4.0 amps was applied to the anode and cathode.

[0084] The results are summarized in Table II. All data recorded was taken after operating the electrolytic reactor for about 3 hours. The measured parameters for each cassette included cassette voltage, current, pressure drop through the bed flow rate (mL/min), ClO_2 concentration (ppm), temperature (°C) and pH.

[t1]

Table II

	Catalyst Material	Cation Exchange Resin
ClO_2 concentration, (ppm)	558	11
Flow Rate, (mL/min)	150	158
Temperature, (°C)	26.5	26.5
pH	2.76	2.45
Pressure Drop, (psi)	8.0	13.0
Voltage, (volts)	23.0	19.2
Current, (Amps)	4.03	4.12

[0085] Clearly, the use of the ceramic catalyst material resulted in significantly superior results compared to the use of cation exchange resin in the central compartment. After only 3 hours of operation, conversion of chlorite ions to chlorine dioxide concentration was 50 times greater with the cassette employing the catalyst bed compared to the cassette employing the cation exchange resin bed. Moreover, the pressure drop across the bed increased significantly with the cassette employing the cation exchange resin indicating compaction of the bed.

Example 5.

[0086] In this example, electrochemical reactor cassettes were configured as described in Figures 4 and 5. The cathode compartment was separated from the central compartment with a cation exchange membrane. The central compartment contained a particulate material bed of three equal layers. The first layer consisted of SK116 cation exchange resin; the second layer consisted of equal amounts by weight of the SK116 cation exchange resin and a catalyst material; and the third layer consisted of the catalyst material. The catalyst material was prepared in accordance with Example 2, i.e., modified SIR-600 resin. The electrode compartments contained SK106 cation exchange resin.

[0087] In one set of cassettes, the anode compartment was separated from the central compartment using a Fluortex[®] 9-70/22 non-permselective membrane commercially available from Sefar America, Inc. The Fluortex[®] is a fluorocarbon based membrane, and in this example, had a pore size of 0.070 millimeters. In a second set of cassettes, the anode compartment was separated from the central compartment using a cation exchange membrane.

[0088] The electrochemical reactor cassettes were operated in the following manner. Softened water having a conductivity of about 120 μ S/cm was passed upwardly through the anode compartment at a flow rate of about 150 mL/min. A 25-weight % sodium chlorite solution was added to the effluent of the anode compartment such that the final concentration of sodium chlorite was about 1000 mg/L. The combined sodium chlorite/effluent solution was then passed through the central compartment at a temperature of about 25 °C. In addition, softened water was passed upwardly through the cathode compartment at a flow rate of about 50 mL/min. While passing

the solutions through the various compartments of the reactor, a controlled current of about 4.0 amps was applied to the anode and cathode.

[0089] Figure 8 graphically illustrates the percent conversion of the chlorite ions to chlorine dioxide as a function of time for each set of cassettes. After an initial break-in period of about 200 hours of operation, the conversion efficiency for the cassettes that included the non-permselective membrane is greater than about 80–90% during the period of time monitored. Thus, the use of the non-permselective membrane between the anode compartment and the central compartment in the electrolytic reactor provided a yield that is at about the maximum possible yield. In contrast, the use of cassettes that included a cation exchange membrane (permselective) between the anode compartment and the central compartment exhibited a gradual decrease in conversion efficiency from about 1000 hours to about 2000 hours. Visual examination of the cation exchange membrane after about 2000 hours of operation indicated that oxidation had occurred. The cation exchange membrane exhibited discoloration, cracking, and delamination. In contrast, examination of the non-permselective membrane showed no visual evidence of oxidation.

[0090] Comparing the conversion efficiencies obtained in Figure 8 with the conversion efficiencies presented in Figure 7 illustrates the increased efficiency resulting from the use of the catalyst material prepared in accordance with Example 1 (ceramic media) as compared to the catalyst material in accordance with Example 2 (ion exchange resin).

[0091] Figure 9 graphically illustrates the applied voltage to the cassette as a function of time. The voltage was adjusted during operation of the electrolytic reactor to maintain a controlled current of about 4.0 amps. In the set of cassettes employing the non-permselective membrane, voltage was relatively constant throughout the 2000 hours of operation. In contrast, the voltage was gradually increased in the cassettes employing the cation exchange membrane (permselective). Since heterogeneous membranes such as the cation exchange membrane consist of colloidal ion exchange particles embedded in an inert binder, the gradual increase in voltage is believed to be caused by the oxidation of the ionthe ion exchange particles, which causes the material to swell within the rigid matrix, thereby decreasing the size of the interstices within the membrane and corresponding access to the ionic sites contained therein.

